

TITLE OF INVENTION

Distillation Process for Reducing the Concentration of Dinitrogen Difluoride
and Dinitrogen Tetrafluoride in Nitrogen Trifluoride

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CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the priority benefit of U.S. provisional
patent application 60/462,756, filed April 14, 2003.

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BACKGROUND OF THE INVENTION

1. Field of the Invention.

The present invention relates to a distillation process for reducing
the concentration of the impurities dinitrogen difluoride and dinitrogen
tetrafluoride in nitrogen trifluoride. The process involves distilling the nitrogen
trifluoride in the presence of a compound with a higher normal boiling point
than nitrogen trifluoride and removing as a distillation column overhead
stream nitrogen trifluoride substantially free of said impurities, removing as a
distillation column sidedraw a concentrated stream comprising said
impurities, and removing as a distillation bottom stream said compound with a
higher normal boiling point than nitrogen trifluoride.

2. Description of Related Art.

Various gaseous fluorine-containing compounds are utilized in
manufacturing processes that plasma-etch silicon-type materials in order to
fabricate semiconductor devices. A major use of nitrogen trifluoride (NF₃) is
as a "chemical vapor deposition" (CVD) chamber cleaning gas in
semiconductor device manufacture. CVD chamber cleaning gases are used
to form plasmas which interact with the internal surfaces of semiconductor
fabrication equipment to remove the various undesirable deposits that
accumulate over time.

Perfluorinated chemicals such as NF₃ that are used in
semiconductor manufacturing applications as cleaning gases are more
commonly referred to as "electronic gases". Electronic gases having high
purity are critical for such applications. It is known that even very small
amounts of impurities in these gases that enter semiconductor device

manufacturing tools can result in wide line width and thus less information per device. Moreover, the presence of these impurities, including but not limited to particulates, metals, moisture, and other halocarbons in the plasma etchant or cleaning gases, even when only present in the part-per-million level,
5 increases the defect rate in the production of these high-density integrated circuits. As a result, there has been increasing demand for higher purity etchant and cleaning gases, and an increasing market value for the materials having the required purity. Identification of impurities and methods for their removal consequently represents a significant aspect of preparing the
10 fluorine-containing compounds for these applications.

NF₃ prepared by a variety of methods, such as the method disclosed in US 3,235,474, may contain relatively large amounts of impurities, such as nitrous oxide (N₂O), carbon dioxide (CO₂), dinitrogen difluoride (N₂F₂-cis and/or N₂F₂-trans) and dinitrogen tetrafluoride (N₂F₄). Dinitrogen
15 difluoride and dinitrogen tetrafluoride are particularly undesirable impurities in a nitrogen trifluoride electronic gas product. Under certain conditions and at relatively low concentration, these compounds can form unstable and even explosive compositions. Therefore, in order to obtain high-purity nitrogen trifluoride that is free from dinitrogen difluoride and dinitrogen tetrafluoride for
20 use as an electronic gas, methods allowing for complete removal of such impurities are necessary.

There are a variety of known methods that may be used to reduce N₂F₂, N₂F₄ and other impurities in a NF₃ product, ranging from distillation, chemical and thermal treatments, adsorption on zeolites, silica gel, and
25 activated alumina. Silica gel and activated alumina are known as both adsorbents for removing impurities at low temperature, and as reactants for removing impurities at higher temperatures.

BRIEF SUMMARY OF THE INVENTION

30 The present invention provides distillation processes for reducing fluorinated impurities from NF₃ so as to produce a purified NF₃ product. More specifically, the present invention comprises a process for reducing the concentration of at least one impurity selected from the group consisting of dinitrogen difluoride and dinitrogen tetrafluoride in a first mixture comprising

nitrogen trifluoride and said at least one impurity, said process comprising:
(a) distilling said first mixture in a distillation column in the presence of a
compound having a higher normal boiling point than nitrogen trifluoride; (b)
removing a second mixture comprising said at least one impurity from said
5 distillation column at a point between the top and the bottom of said
distillation column; (c) removing a third mixture comprising said compound
having a higher normal boiling point than nitrogen trifluoride from the bottom
of said distillation column; and (d) removing a nitrogen trifluoride product
having reduced concentration of said at least one impurity from the top of said
10 distillation column.

BRIEF DESCRIPTION OF THE DRAWING(S)

Figure 1 is a schematic diagram of a distillation system that can be
used for practicing an aspect of the present process.

15 Figure 2 is a schematic diagram of a distillation system that can be
used for practicing an aspect of the present process.

DETAILED DESCRIPTION OF THE INVENTION

NF₃, in its separate and pure state, exhibits properties that are
20 valued for integrated circuit manufacturing and is typically used in related
manufacturing steps. The desire for greater precision and consistency of the
effect it has during integrated circuit manufacture has made extremely high
purities critical for such applications. The presence of any other compounds
in the NF₃ is objectionable for most of its intended uses. For example, even a
25 1 part-per-million-molar concentration of another compound would be
considered an impurity in NF₃ where NF₃ is to be sold as a chemical vapor
deposition (CVD) chamber cleaning gas. Processes that allow for
manufacture of NF₃ products having purities that approach 99.999 molar
percent purity are desirable, but processes that provide at least 99.9999
30 molar percent purity for electronic gases applications are preferred.

Analytical methods for gauging such low concentrations of
impurities in NF₃ are available. For example, methods suitable for analyzing
low concentrations of other compounds in NF₃ are disclosed in the 1995
SEMI standards, pages 149-153, SEMI C3.39.91-Standard for Nitrogen
35 Trifluoride, herein incorporated by reference.

Conventional processes for manufacturing NF_3 often produce at least one of N_2F_2 and N_2F_4 as impurities in the NF_3 product stream. By N_2F_2 is meant either the cis isomer (N_2F_2 -cis, herein also referred to as N_2F_2 -c) or the trans isomer (N_2F_2 -trans, herein also referred to as N_2F_2 -t). The presence of such compounds in the NF_3 product is objectionable for most of its intended uses. The ability to separate and recover a NF_3 product that is substantially-free of such impurities is of considerable value. Herein, "substantially-free" means that at least one of the impurities N_2F_2 and N_2F_4 are present in NF_3 in less than 10 ppm-molar concentration, preferably less than 1 ppm-molar, most preferably less than 0.1 ppm-molar.

The physical properties of mixtures comprising NF_3 , N_2F_2 and N_2F_4 are non-ideal and are difficult to model by conventional modeling techniques. The present invention derives from the finding that when mixtures comprising NF_3 and these impurities are distilled in the presence of another compound having a higher normal boiling point than NF_3 , the N_2F_2 and N_2F_4 are effectively concentrated within the lower distillation sections of a distillation column. That is to say, when mixtures comprising NF_3 and these impurities are distilled in the presence of another compound having a higher normal boiling point than NF_3 , the N_2F_2 and N_2F_4 are effectively concentrated within the bottom 50% of the total number of theoretical stages in a distillation column, and more preferably, within the bottom 25% of the total number of theoretical stages in a distillation column.

By another compound having a higher normal boiling point than NF_3 is meant a compound that has a normal boiling point of from about -90°C to about -20°C . Further, it is preferred that the compound having a higher normal boiling point than NF_3 does not react with NF_3 or the fluorinated impurities under the present process conditions. Suitable compounds having a higher normal boiling point than NF_3 of the present process include compounds from the classes: hydrocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, hydrochlorocarbons, perfluorocarbons and organic oxides and inorganic oxides. Representative hydrocarbons include ethane, propane, and propylene. Representative hydrofluorocarbons include methyl fluoride (HFC-41), difluoromethane (HFC-32), 1,1,1-trifluoroethane (HFC-143a), pentafluoroethane (HFC-125), and fluoroethane (HFC-161). Representative hydrochlorofluorocarbons include chlorodifluoromethane.

(HCFC-22). Representative hydrochlorocarbons include methyl chloride (HCC-40). Representative perfluorocarbons include hexafluoroethane (PFC-116). Representative oxides include nitrous oxide (N_2O), carbon dioxide (CO_2), carbonyl fluoride (COF_2), and perfluoroacetyl fluoride (CF_3COF).

- 5 Preferred compounds having a higher normal boiling point than NF_3 of the present process include nitrous oxide (N_2O), chlorodifluoromethane (HCFC-22), difluoromethane (HFC-32), fluoroethane (HFC-161) and methyl fluoride (HFC-41). These compounds may be used alone or in combination with each other as the high boiling compound in the present separation. For example, it
- 10 is known that N_2O forms azeotropic or azeotrope-like compositions with HFC-23. The respective N_2O /HFC-23 azeotropic or azeotrope-like compositions may be employed as the compound having a higher normal boiling point than NF_3 in the present separation.

- More specifically, when NF_3 and said impurities are distilled in the
- 15 presence of the present compounds having a higher normal boiling point than NF_3 , the impurities N_2F_2 and N_2F_4 form a maximum concentration at a point within the distillation columns packed or trayed sections rather than in either the distillation column's bottoms or overhead streams. As such, withdrawing a sidedraw from a point between the top and bottom of the distillation column
- 20 provides a stream higher in concentration of N_2F_2 and N_2F_4 than in the distillation bottoms or overhead, which facilitates removal of said at least one of N_2F_2 and N_2F_4 from the NF_3 product.

- From the standpoint of reducing said impurities from an NF_3 product, it is more economical to reduce said impurities from a stream
- 25 containing a "higher" concentration rather than from a stream having said impurities at a "lower" concentration. By removing and treating a sidestream in which these impurities have been concentrated, known thermal and adsorptive purification processes for separating N_2F_2 and N_2F_4 from NF_3 can be applied to smaller volumes of process material and the associated
- 30 equipment can in turn be smaller and will operate more efficiently. In addition, larger amounts of NF_3 substantially free of impurities may be obtained as a product of the distillation.

- Such a sidedraw also provides a method of limiting or reducing the maximum concentration of these impurities developed within the distillation
- 35 column. N_2F_2 and N_2F_4 are thought to be more reactive than NF_3 , and under

certain conditions and at relatively low concentration, N_2F_2 and N_2F_4 compounds can form unstable and even explosive compositions and it may be desirable to limit their intracolumn concentration for purposes of materials compatibility or process safety. For example, it is generally preferred that the concentration of these compounds be limited to below 2,000 ppm-molar, more preferably to less than 1,000 ppm-molar intracolumn concentration each of N_2F_2 and N_2F_4 .

Several of the compounds that are produced by processes that produce NF_3 are higher boiling than NF_3 . Examples of such compounds include hexafluoroethane (C_2F_6 or PFC-116), sulfur hexafluoride (SF_6), carbon dioxide (CO_2). In addition, compounds higher boiling than NF_3 may be added as extractants in the distillation of a stream comprising NF_3 and CF_4 to enable the separation of the NF_3 and CF_4 . Examples of such higher boiling compounds suitable as extractants are disclosed in US 6,458,249, herein incorporated by reference, and include chlorodifluoromethane ($CHClF_2$ or HCFC-22), difluoromethane (CH_2F_2 or HFC-32), ethane (C_2H_6), fluoroethane (C_2H_5F or HFC-161), methylfluoride (CH_3F or HFC-41), pentafluoroethane (C_2HF_5 or HFC-125) and nitrous oxide (N_2O).

Figure 1 schematically illustrates a system that may be used to perform aspects of the inventive distillation process. A first mixture comprising NF_3 and at least one of N_2F_2 and N_2F_4 is supplied via conduit 1 to distillation column 2. At least one compound higher boiling than NF_3 is also supplied to the distillation column either together with the first mixture, or optionally via an alternate feed point to the column, such as via conduit 3. The overhead distillate from the column is sent via conduit 4 to condenser 5. At least part of the condensed distillate stream is returned to the column 2 as reflux 6. The remainder of the condensed distillate is recovered via conduit 7 as NF_3 product substantially-free of N_2F_2 or N_2F_4 . A stream comprising at least one of N_2F_2 and N_2F_4 is removed from the column 2 as a sidedraw 8 from the column. A stream comprising said at least one compound higher boiling than NF_3 is removed from the column 2 bottoms via conduit 9 and may be recovered as product. Sidedraw 8 may optionally be sent to a process step where said N_2F_2 and N_2F_4 are removed, and said treated sidedraw stream may then optionally be returned to distillation column 2 for further distillation.

Said invention may be practiced in a distillation column run under a variety of temperatures and pressures. The temperatures at the top of the distillation column should be sufficient to allow condensation of the NF_3 at the pressures the column is operated, but it is preferred that the lowest
5 temperature in the column be above the freezing point of said compounds higher boiler than NF_3 . For example, temperatures at the top of the column ranging from -90°C to -50°C are preferred, but lower temperatures at the top of the column may be employed dependent on the higher boiling compounds that may be present.

10 The present invention is conveniently practiced in combination with the process disclosed in US 6,458,249 for removing CF_4 from NF_3 by use of an extractant agent in a distillation process. In said process a stream comprising NF_3 , CF_4 and at least one of N_2F_2 and N_2F_4 can be fed to a first column where said stream is distilled in the presence of an extractant agent.
15 In the presence of said extractant agent, the CF_4 is separated from the NF_3 , with the CF_4 removed in the column distillate. A bottoms streams comprising NF_3 , extractant agent, and at least one of N_2F_2 and N_2F_4 is then sent to a second distillation column. In the second distillation column, in the presence of said extractant agent, said at least one of N_2F_2 and N_2F_4 will exhibit a
20 concentration maximum at an intermediate point within that column and can be removed from the distillation column in a sidedraw stream while NF_3 is recovered as an overhead product. This sidedraw stream may be optionally treated to remove said at least one of N_2F_2 and N_2F_4 and the treated stream may then be optionally returned to the distillation train. The extractant is
25 removed from the second column as a bottoms stream, and is optionally recycled back to the extraction column. If other compounds are present that exit the second column bottoms with the extractant agent, some portion of this bottoms stream may either be purged or optionally treated to remove these other high boilers, with the treated bottoms stream then optionally
30 return to the distillation train.

Figure 2 schematically illustrates a system which can be used to perform aspects of the inventive extractive distillation process. A first mixture comprising PFC-14, NF_3 and at least one of N_2F_2 and N_2F_4 is supplied via conduit 10 to distillation column 11. At least one extractive entraining agent,
35 e.g., HCFC-22, is supplied via conduit 12 to distillation column 11 at a feed

point higher up the distillation column than the feed point of the mixture to be separated, e.g., PFC-14 and NF_3 . The overhead distillate from the column is sent via conduit 13 to condenser 14. At least part of the condensed distillate stream is returned to the column 11 as reflux 15. The remainder of the condensed distillate is recovered via conduit 16 as PFC-14 product substantially-free of NF_3 , HCFC-22 and said at least one of N_2F_2 and N_2F_4 .

A stream comprising HCFC-22, NF_3 substantially-free of PFC-14, and said at least one of N_2F_2 and N_2F_4 is then removed from the column 11 bottoms via conduit 17 and sent to cooler 18 and from there fed to distillation column 19. The distillate from column 19 may be fed via conduit 20 to condenser 21. From condenser 21, some amount of condensed distillate may be returned to the column 19 as reflux via conduit 22, while the remainder recovered as product, e.g., as NF_3 substantially-free of PFC-14, extractive entraining agent, and at least one of N_2F_2 and N_2F_4 via conduit 23. A stream comprising at least one of N_2F_2 and N_2F_4 is removed from the column 19 as a sidedraw 24 from the column. Extractive entraining agent, e.g., HCFC-22, with the concentration of non-HCFC-22 compounds reduced compared to their concentrations in stream 17 is obtained as the distillation column bottoms 25. Stream 25 may optionally be fed to cooler 26 and then returned to distillation column 11 as extractant feed, fed to the column at a feed point higher up the column than that feed point of the first mixture to be separated, e.g., PFC-14 and NF_3 .

The present invention is optionally practiced in combination with known processes for removing N_2F_2 from a stream comprising NF_3 . For example, a side-draw stream comprising N_2F_2 can be treated by passing the side-draw stream through a heated zone consisting of particulate metal, or packed with solid fluorides to decompose and thus remove said N_2F_2 , methods such as those disclosed in US 4,193,976 and US 5,183,647. The treated side-draw stream may then be optionally returned to the distillation train. The current invention provides an advantage over the prior art, in that the N_2F_2 is concentrated into a small stream which increases the efficiency and economy of the previously disclosed processes.

The present invention may be practiced on a stream comprising N_2F_2 and N_2F_4 where said impurities occur over a range of initial concentrations. For example, said invention may be practiced on a first

mixture where N_2F_2 and N_2F_4 are present in concentrations as high as 10,000 ppm-molar. However, it is preferred that the N_2F_2 and N_2F_4 concentrations in the first mixture be less than 5,000 ppm-molar, more preferably less than 2,000 ppm-molar. Where the initial concentrations of N_2F_2 are higher, said invention is conveniently optionally practiced in combination with known processes for removing N_2F_2 from a stream comprising NF_3 . For example, a first mixture comprising NF_3 and N_2F_2 can be treated by passing the side-draw stream through a heated zone consisting of particulate metal, or packed with solid fluorides to decompose and thus reduce the concentration of said N_2F_2 prior to practicing the present invention.

EXAMPLES

To determine the relative volatility of any given two compounds in a distillation, the PTx Method is preferred. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant temperature for various compositions of the two compounds. Use of the PTx Method is described in greater detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126; the entire disclosure of which is hereby incorporated by reference.

These measurements can be converted into equilibrium vapor and liquid compositions in the PTx cell by using an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase nonidealities. Use of an activity coefficient equation, such as the NRTL equation is described in greater detail in "The Properties of Gases and Liquids," 4th edition, published McGraw Hill, written by Reid, Prausnitz and Poling, on pages 241 and 387, and in "Phase Equilibria in Chemical Engineering," published by Butterworth Publishers, 1985, written by Stanley M. Walas, pages 165 to 244; the entire disclosure of each of the previously identified references are hereby incorporated by reference.

Without wishing to be bound by any theory or explanation, it is believed that the NRTL equation, together with the PTx cell data, can sufficiently predict whether or not combinations of compounds described herein behave in an ideal manner, and can sufficiently predict the relative volatilities of the components in such mixtures during a distillation.

The following examples are provided to illustrate certain aspects of the present invention, and are not intended to limit the scope of the invention. The following examples employ the NRTL equations identified above. In the following examples, each stage is based upon a 100% operational or performance efficiency. The total stages include condenser and reboiler, with the condenser counted as stage No. 1, and the reboiler as the highest numbered stage. In the following examples, flow rates are given in pounds(weight)-per-hour(pph); temperatures are expressed in degrees Celsius (°C.); pressures are expressed in pound-per-square-inch-absolute (psia); stream concentrations are expressed in mole percent (mole %) or parts-per-billion-by-moles (ppbm or ppb-molar).

Comparative Example 1

In this comparative example, a crude NF_3 feed stream comprising NF_3 and N_2F_2 -c, N_2F_2 -t, and N_2F_4 as impurities is fed to a distillation column operated under the conditions shown in Table 1. The concentrations of the N_2F_2 -c, N_2F_2 -t and N_2F_4 in the feed stream are 1,000 ppm-molar each. The column in this comparative example is operated to remove the NF_3 from the column as an overhead distillate, while recovering the impurities as column bottoms. The results of this distillation are shown in Table 1.

TABLE 1			
CASE NUMBER	1	2	3
# of Stages	42	42	42
Crude Feed Stage	30	30	30
Column Top Temperature (°C)	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75
Distillate Temperature (°C)	-75	-75	-75
Bottoms Temperature (°C)	-51	-66	-72
Crude Feed Temperature (°C)	-60	-60	-60
Top Pressure (psia)	215	215	215
Condenser Pressure (psia)	215	215	215
Bottoms Pressure (psia)	217	217	217
Overhead Takeoff Rate (PPH)	99.65	99.20	97.20
Reflux Rate (PPH)	2000.00	2000.00	2000.00
Bottoms Takeoff Rate (PPH)	0.35	0.80	2.80

Crude NF₃ Feed			
NF ₃ (PPH)	99.70	99.70	99.70
N ₂ F ₂ -c (PPH)	0.10	0.10	0.10
N ₂ F ₂ -t (PPH)	0.10	0.10	0.10
N ₂ F ₄ (PPH)	0.10	0.10	0.10
Overhead Takeoff			
NF ₃ (PPH)	99.65	99.20	97.20
N ₂ F ₂ -c (PPH)	0.00000	0.00000	0.00000
N ₂ F ₂ -t (PPH)	0.00000	0.00000	0.00000
Overhead NF₃ Product Composition			
N ₂ F ₂ -c (PPB-MOLAR)	0.001	0.000	0.000
N ₂ F ₂ -t (PPB-MOLAR)	8.809	0.991	0.356
TOT IMP (PPB-MOLAR)	8.810	0.991	0.356
NF ₃ (MOLE %)	100.000	100.000	100.000
Bottoms Takeoff			
NF ₃ (PPH)	0.0500	0.5000	2.5000
N ₂ F ₂ -c (PPH)	0.1000	0.1000	0.1000
N ₂ F ₂ -t (PPH)	0.1000	0.1000	0.1000
N ₂ F ₄ (PPH)	0.1000	0.1000	0.1000
Maximum Internal Concentrations & Stage at Which It Occurs			
N ₂ F ₂ -c (MOLE %)	32.6000	13.7000	3.8600
MAX N ₂ F ₂ -c STAGE NO.	41	42	42
N ₂ F ₂ -t (MOLE %)	36.7000	13.7000	3.8600
MAX N ₂ F ₂ -t STAGE NO.	41	42	42
N ₂ F ₄ (MOLE %)	20.5000	8.7100	2.4500
MAX N ₂ F ₄ STAGE NO.	42	42	42
COLUMN DIAMETER (IN)			
	8	8	8

Under the conditions shown in Table 1, the point of maximum concentration of each of the N₂F₂-cis, N₂F₂-trans, and N₂F₄ are at around stages 41 and 42, or more specifically at around the reboiler or bottoms draw of the distillation column. Increasing the bottoms takeoff rate and changing the reboiler temperatures does not change this point of maximum concentration.

Comparative Example 2

In this comparative example, a crude NF₃ feed stream comprising NF₃ and hexafluoroethane (PFC-116), and N₂F₂-c, N₂F₂-t, and N₂F₄ as

- impurities, is fed to a distillation column operated under the conditions shown in Table 2. The concentrations of the N_2F_2 -c, N_2F_2 -t and N_2F_4 in the feed stream are 1,000 ppm-molar each. The column in this comparative example is operated to remove the NF_3 from the column as an overhead distillate, while recovering the impurities as column bottoms. In this comparative example, there is no material removed as a sidedraw stream. The results of this distillation are shown in Table 2.

TABLE 2			
CASE NUMBER	4	5	6
# of Stages	42	42	42
Crude Feed Stage	30	30	30
Vapor Side-Draw Stage	35	35	35
Column Top Temperature (°C)	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75
Distillate Temperature (°C)	-75	-75	-75
Bottoms Temperature (°C)	-9	-11	-17
Crude Feed Temperature (°C)	-60	-60	-60
Top Pressure (psia)	215	215	215
Condenser Pressure (psia)	215	215	215
Bottoms Pressure (psia)	217	217	217
Overhead Takeoff Rate (PPH)	99.65	99.20	97.20
Reflux Rate (PPH)	2000.00	2000.00	2000.00
Bottoms Takeoff Rate (PPH)	50.35	50.80	52.80
Vapor Sidedraw Rate (PPH)	0.00	0.00	0.00
Crude NF_3 Feed			
NF_3 (PPH)	99.70	99.70	99.70
F116 (PPH)	50.00	50.00	50.00
N_2F_2 -c (PPH)	0.10	0.10	0.10
N_2F_2 -t (PPH)	0.10	0.10	0.10
N_2F_4 (PPH)	0.10	0.10	0.10
Overhead Takeoff			
NF_3 (PPH)	99.65	99.20	97.20
N_2F_2 -c (PPH)	0.00000	0.00000	0.00000
N_2F_2 -t (PPH)	0.00005	0.00000	0.00000
Overhead NF_3 Product Composition			
N_2F_2 -c (PPB-MOLAR)	0.251	0.005	0.001
N_2F_2 -t (PPB-MOLAR)	574.047	23.133	2.585

TOT IMP (PPB-MOLAR)	574.298	23.139	2.586
NF ₃ (MOLE %)	100.000	100.000	100.000
Bottoms Takeoff			
NF ₃ (PPH)	0.0500	0.5000	2.5000
F116 (PPH)	50.0000	50.0000	50.0000
N ₂ F ₂ -c (PPH)	0.0997	0.1000	0.1000
N ₂ F ₂ -t (PPH)	0.0994	0.0999	0.1000
N ₂ F ₄ (PPH)	0.1000	0.1000	0.1000
Column Sidedraw			
NF ₃ (PPH)	0.0000	0.0000	0.0000
F116 (PPH)	0.0000	0.0000	0.0000
N ₂ F ₂ -c (PPH)	0.0000	0.0000	0.0000
N ₂ F ₂ -t (PPH)	0.0000	0.0000	0.0000
N ₂ F ₄ (PPH)	0.0000	0.0000	0.0000
Maximum Internal Concentrations & Stage at Which It Occurs			
N ₂ F ₂ -c (MOLE %)	36.2000	17.7000	4.8500
MAX N ₂ F ₂ -c STAGE NO.	37	38	39
N ₂ F ₂ -t (MOLE %)	42.1000	19.6000	5.5700
MAX N ₂ F ₂ -t STAGE NO.	34	37	39
N ₂ F ₄ (MOLE %)	0.3380	0.3050	0.2460
MAX N ₂ F ₄ STAGE NO.	40	40	41
COLUMN DIAMETER (IN)	8	8	8

- In contrast to comparative example 1, the presence of PFC-116 in this comparative example causes the point of maximum concentration for each of N₂F₂-c, N₂F₂-t and N₂F₄ to occur at higher points in the distillation column. Without a sidedraw stream, the column concentration of each increase significantly, up to 42.1 mole % in one case, before these impurities appear in the bottom stream and can be removed from the column.

Example 1

- This example is identical to comparative example 1, with the exception that a 4 pph sidedraw is removed from the distillation column at stage 35. The results of this distillation are shown in Table 3.

TABLE 3			
CASE NUMBER	7	8	9

# of Stages	42	42	42
Crude Feed Stage	30	30	30
Vapor Side-Draw Stage	35	35	35
Column Top Temperature (°C)	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75
Distillate Temperature (°C)	-75	-75	-75
Bottoms Temperature (°C)	-8	-10	-17
Crude NF ₃ Feed Temperature (°C)	-60	-60	-60
Top Pressure (psia)	214.7	214.7	214.7
Condenser Pressure (psia)	214.7	214.7	214.7
Bottoms Pressure (psia)	216.7	216.7	216.7
Overhead Takeoff Rate (PPH)	96.11	95.38	93.26
Reflux Rate (PPH)	2000.00	2000.00	2000.00
Bottoms Takeoff Rate (PPH)	49.89	50.62	52.74
Vapor Sidedraw Rate (PPH)	4.00	4.00	4.00
Crude NF₃ Feed			
NF ₃ (PPH)	99.70	99.70	99.70
F116 (PPH)	50.00	50.00	50.00
N ₂ F ₂ -c (PPH)	0.10	0.10	0.10
N ₂ F ₂ -t (PPH)	0.10	0.10	0.10
N ₂ F ₄ (PPH)	0.10	0.10	0.10
Overhead Takeoff			
NF ₃ (PPH)	96.11	95.38	93.26
N ₂ F ₂ -c (PPH)	0.00000	0.00000	0.00000
N ₂ F ₂ -t (PPH)	0.00000	0.00000	0.00000
Overhead NF₃ Product Composition			
N ₂ F ₂ -c (PPB-MOLAR)	0.004	0.002	0.000
N ₂ F ₂ -t (PPB-MOLAR)	7.405	5.271	1.841
TOT IMP (PPB-MOLAR)	7.408	5.273	1.842
NF ₃ (MOLE %)	100.000	100.000	100.000
Bottoms Takeoff			
NF ₃ (PPH)	0.0500	0.5000	2.5000
F116 (PPH)	49.7380	49.9710	49.9810
N ₂ F ₂ -c (PPH)	0.0006	0.0313	0.0893
N ₂ F ₂ -t (PPH)	0.0006	0.0183	0.0719
N ₂ F ₄ (PPH)	0.0983	0.1000	0.1000
Column Sidedraw			
NF ₃ (PPH)	3.5377	3.8202	3.9418
F116 (PPH)	0.2618	0.0294	0.0194
N ₂ F ₂ -c (PPH)	0.0994	0.0687	0.0107

N ₂ F ₂ -t (PPH)	0.0994	0.0817	0.0281
N ₂ F ₄ (PPH)	0.0017	0.0000	0.0000
Maximum Internal Concentrations & Stage at Which It Occurs			
N ₂ F ₂ -c (MOLE %)	3.5100	9.2100	4.4800
MAX N ₂ F ₂ -c STAGE NO.	35	37	39
N ₂ F ₂ -t (MOLE %)	2.9000	5.8900	4.1200
MAX N ₂ F ₂ -t STAGE NO.	35	37	39
N ₂ F ₄ (MOLE %)	0.4650	0.3230	0.2470
MAX N ₂ F ₄ STAGE NO.	37	40	41
COLUMN DIAMETER (IN)	8	8	8

- This example shows how a sidedraw stream may be used to remove N₂F₂-t, N₂F₂-c and N₂F₄ from the column, and so reduce the concentration of each developed. The points of maximum concentration of each is still at a higher point than in comparative example 1, but the maximum concentrations of N₂F₂-c and N₂F₂-t are considerably reduced compared to comparative example 2.

Comparative Example 3

- In this comparative example, a crude NF₃ feed stream comprising NF₃ and hexafluoroethane (PFC-116) and N₂F₂-c, N₂F₂-t, and N₂F₄ as impurities is fed to a distillation column operated under the conditions shown in Table 4. The concentrations of the N₂F₂-c, N₂F₂-t and N₂F₄ in the feed stream are 1000 ppm-molar each. The feed rate of PFC-116 is 5000 pph.
- The column in this example is operated to remove the NF₃ from the column as an overhead distillate, while recovering the impurities as column bottoms. In this comparative example, there is no material removed as a sidedraw stream. The results of this distillation are shown in Table 4.

<u>TABLE 4</u>			
<u>CASE NUMBER</u>	<u>10</u>	<u>11</u>	<u>12</u>
# of Stages	42	42	42
Crude Feed Stage	30	30	30
Vapor Side-Draw Stage	35	35	35
Column Top Temperature (°C)	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75

Distillate Temperature (°C)	-75	-75	-75
Bottoms Temperature (°C)	-8	-8	-8
Crude Feed Temperature (°C)	-60	-60	-60
Top Pressure (psia)	214.7	214.7	214.7
Condenser Pressure (psia)	214.7	214.7	214.7
Bottoms Pressure (psia)	216.7	216.7	216.7
Overhead Takeoff Rate (PPH)	99.83	99.20	97.19
Reflux Rate (PPH)	5000.00	5000.00	5000.00
Bottoms Takeoff Rate (PPH)	5000.12	5000.75	5002.76
Vapor Sidedraw Rate (PPH)	0.00	0.00	0.00
Crude NF₃ Feed			
NF ₃ (PPH)	99.70	99.70	99.70
F116 (PPH)	5000.00	5000.00	5000.00
N ₂ F ₂ -c (PPH)	0.10	0.10	0.10
N ₂ F ₂ -t (PPH)	0.10	0.10	0.10
N ₂ F ₄ (PPH)	0.10	0.10	0.10
Overhead Takeoff			
NF ₃ (PPH)	99.65	99.2	97.19
F116 (PPH)	0.00000	0.00000	0.00000
N ₂ F ₂ -c (PPH)	0.08330	0.00000	0.00000
N ₂ F ₂ -t (PPH)	0.09940	0.00044	0.00004
Overhead NF₃ Product Composition			
F116 (PPB-MOLAR)	3.232	0.000	0.000
N ₂ F ₂ -c (PPB-MOLAR)	897199.403	17.664	0.862
N ₂ F ₂ -t (PPB-MOLAR)	1070901.558	4752.819	435.402
TOT IMP (PPB-MOLAR)	1968104.193	4770.483	436.264
NF ₃ (MOLE %)	99.803	100.000	100.000
Bottoms Takeoff			
NF ₃ (PPH)	0.0500	0.5000	2.5000
F116 (PPH)	4999.9490	4999.9550	4999.9640
N ₂ F ₂ -c (PPH)	0.0165	0.0985	0.0987
N ₂ F ₂ -t (PPH)	0.0006	0.0989	0.0993
N ₂ F ₄ (PPH)	0.1000	0.1000	0.1000
Column Sidedraw			
NF ₃ (PPH)	0.0000	0.0000	0.0000
F116 (PPH)	0.0000	0.0000	0.0000
N ₂ F ₂ -c (PPH)	0.0000	0.0000	0.0000
N ₂ F ₂ -t (PPH)	0.0000	0.0000	0.0000
N ₂ F ₄ (PPH)	0.0000	0.0000	0.0000

Maximum Internal Concentrations & Stage at Which It Occurs			
N ₂ F ₂ -c (MOLE %)	86.2000	40.2000	17.5000
MAX N ₂ F ₂ -c STAGE NO.	22	28	29
N ₂ F ₂ -t (MOLE %)	6.8800	30.9000	15.3000
MAX N ₂ F ₂ -t STAGE NO.	12	26	28
N ₂ F ₄ (MOLE %)	0.0041	0.0039	0.0037
MAX N ₂ F ₄ STAGE NO.	34	36	37
COLUMN DIAMETER (IN)	8	8	8

- In this comparative example, the feed rate of PFC-116 relative to that of NF₃ in the crude feed stream is comparable to what would appear in a stripper column having no side draw, said stripper column following an
- 5 extractive distillation column using 116 as the extractant. The increase in PFC-116 fed versus comparative example 2 causes the points of maximum concentration of each of the N₂F₂-c, N₂F₂-t and N₂F₄ to shift even further up the distillation column, and causes a substantial increase in the intracolumn concentration maximum of N₂F₂-c and N₂F₂-t versus comparative example 2.
- 10 Combined, these cause a significant increase in the concentration of each of N₂F₂-c, N₂F₂-t and N₂F₄ in the NF₃ product in the column distillate.

Example 2

- This Example is identical to comparative example 3, except that
- 15 there is now a 10 pph sidedraw and the number of stages has been increased from 42 to 62. The results of this distillation may be seen in Table 5.

<u>TABLE 5</u>			
<u>CASE NUMBER</u>	<u>13</u>	<u>14</u>	<u>15</u>
# of Stages	62	62	62
Crude Feed Stage	45	45	45
Vapor Side-Draw Stage	50	50	50
Column Top Temperature (°C)	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75
Distillate Temperature (°C)	-75	-75	-75
Bottoms Temperature (°C)	-8	-8	-8
Crude NF ₃ Feed Temperature (°C)	-60	-60	-60

Top Pressure (psia)	215	215	215
Condenser Pressure (psia)	215	215	215
Bottoms Pressure (psia)	217	217	217
Overhead Takeoff Rate (PPH)	98.86	94.53	89.98
Reflux Rate (PPH)	5000.00	5000.00	5000.00
Bottoms Takeoff Rate (PPH)	4991.14	4995.47	5000.02
Vapor Sidedraw Rate (PPH)	10.00	10.00	10.00
Crude NF₃ Feed			
NF ₃ (PPH)	99.70	99.70	99.70
F116 (PPH)	5000.00	5000.00	5000.00
N ₂ F ₂ -c (PPH)	0.10	0.10	0.10
N ₂ F ₂ -t (PPH)	0.10	0.10	0.10
N ₂ F ₄ (PPH)	0.10	0.10	0.10
Overhead Takeoff			
NF ₃ (PPH)	98.86000	94.53000	89.98000
N ₂ F ₂ -c (PPH)	0.00000	0.00000	0.00000
N ₂ F ₂ -t (PPH)	0.00000	0.00000	0.00000
Overhead NF₃ Product Composition			
N ₂ F ₂ -c (PPB-MOLAR)	0.000	0.000	0.000
N ₂ F ₂ -t (PPB-MOLAR)	0.496	0.048	0.024
TOT IMP (PPB-MOLAR)	0.496	0.048	0.024
NF ₃ (MOLE %)	100	100	100
Bottoms Takeoff			
NF ₃ (PPH)	0.0500	0.5000	2.5000
F116 (PPH)	4990.9880	4994.8650	4997.4100
N ₂ F ₂ -c (PPH)	0.0005	0.0007	0.0034
N ₂ F ₂ -t (PPH)	0.0016	0.0016	0.0044
N ₂ F ₄ (PPH)	0.0996	0.0998	0.0999
Column Sidedraw			
NF ₃ (PPH)	0.7902	4.6670	7.2175
F116 (PPH)	9.0115	5.1351	2.5903
N ₂ F ₂ -c (PPH)	0.0995	0.0993	0.0966
N ₂ F ₂ -t (PPH)	0.0984	0.0984	0.0956
N ₂ F ₄ (PPH)	0.0004	0.0002	0.0001
Maximum Internal Concentrations & Stage at Which It Occurs			
N ₂ F ₂ -c (MOLE %)	13.8000	1.8700	0.9480
MAX N ₂ F ₂ -c STAGE NO.	44	44	44
N ₂ F ₂ -t (MOLE %)	19.9000	3.5000	1.9100
MAX N ₂ F ₂ -t STAGE NO.	43	44	44

N ₂ F ₄ (MOLE %)	0.0042	0.0040	0.0037
MAX N ₂ F ₄ STAGE NO.	52	55	56
COLUMN DIAMETER (IN)	8	8	8

This example shows how a sidedraw stream may be used to remove N₂F₂-t, N₂F₂-c and N₂F₄ from the column, and so reduce the concentration of each developed. The combination of increased column stages and sidedraw also allow NF₃ substantially free of impurities to be obtained as column distillate.

Comparative Example 4

In this comparative example, a crude NF₃ feed stream comprising NF₃ and N₂F₂-c, N₂F₂-t, and N₂F₄ as impurities is fed to a distillation column operated under the conditions shown in Table 6. The concentrations of the N₂F₂-c, N₂F₂-t and N₂F₄ in the feed stream are 1,000 ppm-molar each. In case number 15, no additional high boiling compound is fed. In case numbers 16, 17, 18, 19 and 20 the additional high boilers PFC-116, HCFC-22, HFC-23, HFC-32 and HFC-125 respectively are also fed to the column in the crude NF₃ feed steam. The column in this comparative example is operated to remove the NF₃ from the column as an overhead distillate, while recovering the impurities as column bottoms. In this comparative example, there is no material removed as a sidedraw stream. The results of this distillation are shown in Table 6.

<u>Table 6</u>						
<u>CASE NUMBER</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>
<u>High Boiler</u>	None	PFC-116	HCFC-22	HFC-23	HFC-32	HFC-125
# of Stages	42	42	42	42	42	42
Crude Feed Stage	30	30	30	30	30	30
Vapor Sidedraw Stage	35	35	35	35	35	35
Column Top Temperature (°C)	-75	-75	-75	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75	-75	-75	-75
Distillate Temperature (°C)	-75	-75	-75	-75	-75	-75
Bottoms Temperature (°C)	-51	-9	36	-19	18	26
Crude Feed Temperature (°C)	-60	-60	-60	-60	-60	-60

Top Pressure (psia)	215	215	215	215	215	215
Condenser Pressure (psia)	215	215	215	215	215	215
Bottoms Pressure (psia)	217	217	217	217	217	217
Overhead Takeoff Rate (PPH)	99.65	99.65	99.65	99.65	99.65	99.65
Reflux Rate (PPH)	2000.00	2000.00	2000.00	2000.00	2000.00	2000.00
Bottoms Takeoff Rate (PPH)	0.35	50.35	50.35	50.35	50.35	50.35
Vapor Sidedraw Rate (PPH)	0.00	0.00	0.00	0.00	0.00	0.00
Crude NF₃ Feed						
NF ₃ (PPH)	99.70	99.70	99.70	99.70	99.70	99.70
High Boiler (PPH)	-----	50.00	50.00	50.00	50.00	50.00
N ₂ F ₂ -c (PPH)	0.10	0.10	0.10	0.10	0.10	0.10
N ₂ F ₂ -t (PPH)	0.10	0.10	0.10	0.10	0.10	0.10
N ₂ F ₄ (PPH)	0.10	0.10	0.10	0.10	0.10	0.10
Overhead Takeoff						
NF ₃ (PPH)	99.65	99.65	99.65	99.65	99.65	99.65
N ₂ F ₂ -c (PPH)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N ₂ F ₂ -t (PPH)	0.00000	0.00005	0.00000	0.00000	0.00000	0.00000
High Boiler (PPH)	-----	0.00000	0.00000	0.00000	0.00000	0.00000
Overhead NF₃ Product Compositions						
N ₂ F ₂ -c (PPB-MOLAR)	0.001	0.251	0.004	0.009	0.004	0.007
N ₂ F ₂ -t (PPB-MOLAR)	8.809	574.047	17.943	35.429	16.086	24.168
High Boiler (PPB-MOLAR)	-----	0.000	0.000	28.205	0.000	0.000
TOT IMP (PPB-MOLAR)	8.810	574.298	17.947	63.644	16.090	24.175
NF ₃ (MOLE %)	100.000	100.000	100.000	100.000	100.000	100.000
Bottoms Takeoff						
NF ₃ (PPH)	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500
High Boiler (PPH)	-----	50.0000	50.0000	50.0000	50.0000	50.0000
N ₂ F ₂ -c (PPH)	0.1000	0.0997	0.1000	0.0999	0.0999	0.0999
N ₂ F ₂ -t (PPH)	0.1000	0.0994	0.0999	0.0998	0.0999	0.0999
N ₂ F ₄ (PPH)	0.1000	0.1000	0.1000	0.1000	0.1000	0.1000
Column Sidedraw						
NF ₃ (PPH)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
High Boiler (PPH)	-----	0.0000	0.0000	0.0000	0.0000	0.0000
N ₂ F ₂ -c (PPH)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N ₂ F ₂ -t (PPH)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N ₂ F ₄ (PPH)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Maximum Internal Concentrations & Stage at Which It Occurs						
N ₂ F ₂ -c (MOLE %)	32.6000	36.2000	32.7000	20.8000	31.6000	32.8000
MAX N ₂ F ₂ -c STAGE NO.	41	37	39	37	39	38
N ₂ F ₂ -t (MOLE %)	36.7000	42.1000	30.0000	24.6000	29.2000	28.8000
MAX N ₂ F ₂ -t STAGE NO.	41	34	39	37	39	38
N ₂ F ₄ (MOLE %)	20.5000	0.3380	2.1500	0.1530	1.6300	1.0900
MAX N ₂ F ₄ STAGE NO.	42	40	40	40	40	39

Column Diameter (inches)	8	8	8	8	8	8

In contrast to case number 15 of table 6, where no additional high boiler is fed, the presence of the high boilers is case numbers 16 through 20 of table 6 cause the point of maximum concentration for each of N₂F₂-c, N₂F₂-t and N₂F₄ to occur at higher points in the distillation column.

Example 3

This example is identical to case numbers 16 through 20 of comparative example 4, except that there is now a 4 pph sidedraw. The results of this distillation may be seen in Table 7.

<u>Table 7</u>					
<u>CASE NUMBER</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>
High Boiler	PFC-116	HCFC-22	HFC-23	HFC-32	HFC-125
# of Stages	42	42	42	42	42
Crude Feed Stage	30	30	30	30	30
Vapor Sidedraw Stage	35	35	35	35	35
Column Top Temperature (°C)	-75	-75	-75	-75	-75
Reflux Temperature (°C)	-75	-75	-75	-75	-75
Distillate Temperature (°C)	-75	-75	-75	-75	-75
Bottoms Temperature (°C)	-8	37	-18	19	27
Crude Feed Temperature (°C)	-60	-60	-60	-60	-60
Top Pressure (psia)	215	215	215	215	215
Condenser Pressure (psia)	215	215	215	215	215
Bottoms Pressure (psia)	217	217	217	217	217
Overhead Takeoff Rate (PPH)	96.11	95.80	95.98	95.82	95.81
Reflux Rate (PPH)	2000.00	2000.00	2000.00	2000.00	2000.00
Bottoms Takeoff Rate (PPH)	49.89	50.20	50.02	50.18	50.19
Vapor Sidedraw Rate (PPH)	4.00	4.00	4.00	4.00	4.00
<u>Crude NF₃ Feed</u>					
NF ₃ (PPH)	99.70	99.70	99.70	99.70	99.70
High Boiler (PPH)	50.00	50.00	50.00	50.00	0.10
N ₂ F ₂ -c (PPH)	0.10	0.10	0.10	0.10	0.10
N ₂ F ₂ -t (PPH)	0.10	0.10	0.10	0.10	0.10
N ₂ F ₄ (PPH)	0.10	0.10	0.10	0.10	50.00

PCT Text

Overhead Takeoff					
NF ₃ (PPH)	96.11	95.80	95.98	95.82	95.81
N ₂ F ₂ -c (PPH)	0.00000	0.00000	0.00000	0.00000	0.00000
N ₂ F ₂ -t (PPH)	0.00000	0.00000	0.00000	0.00000	0.00000
High Boiler (PPH)	0.00000	0.00000	0.00000	0.00000	0.00000
Overhead NF₃ Product Compositions					
N ₂ F ₂ -c (PPB-MOLAR)	0.004	0.002	0.002	0.001	0.002
N ₂ F ₂ -t (PPB-MOLAR)	7.405	4.346	5.038	3.908	4.556
High Boiler (PPB-MOLAR)	0.000	0.000	25.613	0.000	0.000
TOT IMP (PPB-MOLAR)	7.408	4.347	30.654	3.910	4.558
NF ₃ (MOLE %)	100.000	100.000	100.000	100.000	100.000
Bottoms Takeoff					
NF ₃ (PPH)	0.0500	0.0500	0.0500	0.0500	0.0500
High Boiler (PPH)	49.7380	49.9870	49.8360	49.9550	49.9900
N ₂ F ₂ -c (PPH)	0.0006	0.0408	0.0219	0.0479	0.0283
N ₂ F ₂ -t (PPH)	0.0006	0.0226	0.0125	0.0263	0.0178
N ₂ F ₄ (PPH)	0.0983	0.1000	0.1000	0.1000	0.0999
Column Sidedraw					
NF ₃ (PPH)	3.5377	3.8505	3.6700	3.8290	3.8360
High Boiler (PPH)	0.2618	0.0129	0.1643	0.0452	0.0100
N ₂ F ₂ -c (PPH)	0.0994	0.0592	0.0781	0.0521	0.0717
N ₂ F ₂ -t (PPH)	0.0994	0.0774	0.0875	0.0737	0.0822
N ₂ F ₄ (PPH)	0.0017	0.0000	0.0000	0.0000	0.0001
Maximum Internal Concentrations & Stage at Which It Occurs					
N ₂ F ₂ -c (MOLE %)	3.5100	25.8000	9.5100	25.2000	19.3000
MAX N ₂ F ₂ -C STAGE NO.	35	39	37	39	38
N ₂ F ₂ -t (MOLE %)	2.9000	12.6000	5.8700	13.1000	9.9200
MAX N ₂ F ₂ -t STAGE NO.	35	39	37	39	38
N ₂ F ₄ (MOLE %)	0.4650	2.6800	0.1650	2.0100	1.8800
MAX N ₂ F ₄ STAGE NO.	37	40	39	40	39
Column Diameter (inches)	8	8	8	8	8

This example shows how a sidedraw stream may be used to remove N₂F₂-t, N₂F₂-c and N₂F₄ from the column, and so reduce the maximum concentration of each developed. The points of maximum concentration of each impurity in cases 16 through 25 where a high boiler is added is still at a higher point than in case number 15 where no high boiler is added, but the maximum concentrations of N₂F₂-c and N₂F₂-t are considerably reduced compared to each high boilers respective case in comparative example 4.

CLAIM(S)

What is claimed is :

- 5 1. A process for reducing the concentration of at least one impurity selected from the group consisting of dinitrogen difluoride and dinitrogen tetrafluoride in a first mixture comprising nitrogen trifluoride and said at least one impurity, said process comprising:
- 10 (a) distilling said first mixture in a distillation column in the presence of a compound having a higher normal boiling point than nitrogen trifluoride;
- (b) removing a second mixture comprising said at least one impurity from said distillation column at a point between the top and the bottom of said distillation column;
- 15 (c) removing a third mixture comprising said compound having a higher normal boiling point than nitrogen trifluoride from the bottom of said distillation column; and
- (d) removing a nitrogen trifluoride product having reduced concentration of said at least one impurity from the top of said distillation column.
- 20 2. The process of claim 1 wherein said compound having a higher normal boiling point than nitrogen trifluoride is introduced into said distillation column during said distilling step in the liquid phase at a point in said distillation column above the point at which said first mixture is introduced into said
- 25 distillation column.
3. The process of claim 1 wherein said first mixture comprises up to about 5,000 parts-per-million-molar of said at least one impurity.
- 30 4. The process of claim 1 wherein said compound having a higher normal boiling point than nitrogen trifluoride has a normal boiling point of from about -90°C to about -20°C.
5. The process of claim 4 wherein said compound having a higher normal
- 35 boiling point than nitrogen trifluoride is at least one compound selected from

the group consisting of hydrocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, hydrochlorocarbons, perfluorocarbons, organic oxides and inorganic oxides.

5 6. The process of claim 5 wherein said compound having a higher normal boiling point than nitrogen trifluoride is at least one compound selected from the group consisting of ethane, propane, propylene, methyl fluoride, difluoromethane, fluoroethane, 1,1,1-trifluoroethane, pentafluoroethane, chlorodifluoromethane, methyl chloride, hexafluoroethane, nitrous oxide,
10 carbon dioxide, carbonyl fluoride, trifluoroacetyl fluoride.

7. The process of claim 5 wherein said compound having a higher normal boiling point than nitrogen trifluoride is at least one compound selected from the group consisting of methyl fluoride, difluoromethane, fluoroethane,
15 chlorodifluoromethane, and nitrous oxide.

8. The process of claim 5 wherein said compound having a higher normal boiling point than nitrogen trifluoride is nitrous oxide.

20 9. The process of claim 1 wherein the temperature at the top of said first distillation column during said distilling step is from about -90°C to about -50°C.

10. The process of claim 1 wherein said removing of said second mixture
25 from said distillation column is sufficient to maintain the maximum concentration of said at least one impurity in said distillation column below about 2,000 ppm-molar.

11. The process of claim 1 wherein said point between the top and the
30 bottom of said distillation column is located within the bottom 50% of the total number of theoretical stages in said distillation column.

12. The process of claim 1 wherein said point between the top and the
bottom of said distillation column is located within the bottom 25% of the total
35 number of theoretical stages in said distillation column.

13. The process of claim 1 wherein said nitrogen trifluoride product contains less than about 0.1 parts-per-million-molar of said at least one impurity.

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14. A process for reducing the concentration of at least one impurity selected from the group consisting of dinitrogen difluoride and dinitrogen tetrafluoride in a first mixture comprising nitrogen trifluoride and said at least one impurity, said process comprising:

10 (a) distilling said first mixture in a distillation column in the presence of nitrous oxide;

(b) removing a second mixture comprising said at least one impurity from said distillation column at a point between the top and the bottom of said distillation column;

15 (c) removing a third mixture comprising nitrous oxide from the bottom of said distillation column; and

(d) removing a nitrogen trifluoride product having reduced concentration of said at least one impurity from the top of said distillation column.

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15. A process for reducing the concentration of at least one impurity selected from the group consisting of dinitrogen difluoride and dinitrogen tetrafluoride in a first mixture comprising nitrogen trifluoride and said at least one impurity, said process comprising:

25 (a) distilling said first mixture in a distillation column in the presence of nitrous oxide;

(b) removing a second mixture comprising said at least one impurity from said distillation column at a point between the top and the bottom of said distillation column;

30 (c) removing said at least one impurity from said second mixture to form a third mixture, and feeding said third mixture to said distillation column;

(d) removing a fourth mixture comprising nitrous oxide from the bottom of said distillation column; and

(e) removing a nitrogen trifluoride product having reduced concentration of said at least one impurity from the top of said distillation column.